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THEORETICAL STUDIES OF NUCLEATION KINETICS AND NANODROPLET MICROSTRUCTURE

Final Report

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NOTICE

Project Aims:
The project goals were threefold: (1) to explore ways of bridging the gap between fundamental molecular nucleation theories and phenomenological approaches based on thermodynamic reasoning, (2) to test and improve binary nucleation theory, and (3) to provide the theoretical underpinning for a powerful new experimental technique, small angle neutron scattering (SANS) from nanodroplet aerosols, that can probe the compositional structure of nanodroplets.

Project Results:
DOE funding for this project has totally or partially supported the publication of 17 journal articles, 9 conference proceedings, 1 M.S. thesis and 1 Ph.D. thesis. A complete list of these is located at the end of this report. Broadly speaking, the subjects of these papers fall into three categories: (1) theoretical work on nucleation theory (2) experiments and modeling of nucleation and condensation in supersonic nozzles, and (3) experimental and theoretical work on nanodroplet structure and neutron scattering. The paper numbers noted by each research topic refer to the list at the end of this report.

1. Nucleation Theory

Quasi-universal behavior of binary nucleation kinetics (No. 1 and 2) The main result of this work was the realization that the quasi-universal appearance of the normalized concentration pattern for a given binary system was controlled primarily by the distribution of cluster decay rates (evaporation rates) as a function of cluster composition. Because the cluster evaporation rates depend weakly on the gas phase composition, a single plot of evaporation rates versus cluster composition can characterize the behavior of a given binary system over the entire system composition range. The results of this work were published as two papers in the *Journal of Chemical Physics*.

Scaled theory of binary nucleation (No. 3) A new scaled theory of binary nucleation was developed for ideal systems. This approach casts the nucleation rate in terms of dimensionless, material independent parameters whose values are universal constants, at least for similar classes of materials. The approach worked well when applied to ideal mixtures of alcohols. The work was published in *Chemical Physics Letters*.

Major pathway for nucleation flux in binary systems (No. 6 and 19) This new approach to the problem of the pathway of binary nucleation replaces the thermodynamic potential by a generalized nucleation potential that is the sum of the thermodynamic potential and several other terms of kinetic origin. This potential always contains a saddle point through which the major nucleation flux passes. Most of the time, this saddle point, termed the genuine saddle point or GSP, is essentially identical to the thermodynamic saddle point or TSP of the conventional theory, but when nucleation occurs by means of ridge crossing, the GSP and TSP differ greatly. This work was published as a *Rapid Communication* in the *Physical Review E*.

Temperature dependence of binary nucleation rates (No. 8)
Numerical and analytical studies of binary nucleation kinetics were performed with a new self-consistent version of binary nucleation theory based on the Kelvin equation to determine cluster evaporation rates. The new model provides a better representation of the temperature dependence of the binary nucleation rate than any other classical model. This work was published in the *Journal of Physical Chemistry B*.

Monte Carlo simulations of small methanol clusters (No. 27)
Monte Carlo computer simulations of small molecular clusters were performed to evaluate the free energy of formation needed to estimate nucleation rates. The Bennett Monte Carlo technique and modified Jorgensen effective atom-atom pair potentials were used to calculate Helmholtz free energy differences

for small (n=2 to 200 molecule) methanol clusters for temperatures between 200K and 300K. The Monte Carlo simulations and early results are described in the M.S. thesis of S. M. Raman (2003).

Temperature dependence of nucleation rates from DFT and gradient theory (No. 9) Density functional theory (DFT) and its more approximate form, known as gradient theory (GT) were used to compare the temperature dependence of droplet nucleation rates predicted by these two nonclassical theories of nucleation for a hard-sphere Yukawa (HSY) fluid. For this model, DFT predicts a temperature-dependence for the nucleation rate that agrees well with experimental measurements for many real systems. This work showed that, compared to classical theory, GT also improves the predicted temperature dependence, although not to the same extent as the more comprehensive DFT. This work was published in the *Journal of Chemical Physics*.

Nucleation near the spinodal: Failure of DFT (No. 11) This work investigated the diverging size of the critical nucleus near the spinodal using gradient theory (GT) and mean field density functional theory (MFDFT). GT predicts that at the spinodal the free energy barrier to nucleation vanishes while the radius of the critical fluctuation diverges. The Cahn and Hilliard scaling behavior for these quantities held quantitatively for both GT and MFDFT. The excess number of molecules, Δg, in the critical nucleus also satisfied Cahn-Hilliard scaling near the spinodal. The divergence of Δg is due to the divergence of the mean field isothermal compressibility of the fluid at the spinodal. A Ginzburg criterion for the validity of the mean field scaling relations was developed. For real fluids with short range attractive interactions, the near-spinodal scaling behavior occurs in a fluctuation dominated regime for which MFDFT is invalid. Based on the nucleation theorem and on Wang's (J. Chem. Phys. **117**, 481 (2002)) treatment of fluctuations near the spinodal in polymer blends, a finite size was inferred for the critical nucleus at the pseudospinodal identified by Wang. This prediction is consistent with the recent and controversial experimental results of LeFebvre et al. ((J. Chem. Phys. **116**, 4777 (2002)) which found a finite nucleus near the spinodal for nucleation in polymer blends. This work was published in the *Journal of Chemical Physics*.

Nucleation theory with equations of state (No.12 and 28) Using an accurate equation of state, this work showed that, unlike the approximate form commonly used in classical nucleation theory, the original version of Gibbs's formula for the reversible work of critical nucleus formation predicts the correct temperature dependence of the nucleation rate for both ordinary and heavy water. This is a remarkable and totally unexpected result. This work formed part of the Ph. D. thesis (2003) of A. Obeidat. A full paper describing this work was published in the *Journal of Chemical Physics*.

Binary nucleation in size and composition space (No.13 and 21) An alternative formalism for describing binary nucleation kinetics was developed. The formalism relies on the exact replacement of the two size variables in the most common treatments in favor of an overall size variable and a relative composition variable. This form of the equations makes it easier to explore certain limiting cases, such as droplet growth dynamics far from the saddle point. This work was published in *Physical Review E.*

Bubble nucleation (No.16) A new version of the nucleation theorem was developed which allows the volumes of nanometer-sized critical bubbles to be determined rigorously from measurements of bubble nucleation rates. The new result is valid regardless of the composition or degree of nonideality of the bubble phase, unlike an earlier result. This result was published in the *Journal of Chemical Physics*.

Gradient theory of nucleation in polar fluids (No.17, 26, and 28) Gradient theory (GT), a simpler, approximate form of density functional theory (DFT), was applied to water, methanol, and ethanol using the cubic perturbed hard body (CPHB) equation of state (EOS). Compared to the standard form of classical nucleation theory (CNT), the GT results for water showed improved temperature dependence, but the supersaturation dependence was slightly poorer. The rates predicted by GT for methanol and

ethanol were improved by several orders of magnitude compared to CNT predictions, but the predicted temperature dependence was not significantly improved. This work formed part of the Ph. D. thesis (2003) of A. Obeidat. These results were presented at the 16th International Conference on Nucleation and Atmospheric Aerosols in Kyoto and were published in the proceedings of the latter. A full paper was published in a special issue of the journal, *Atmospheric Research*.

Binary Nucleation of a Nonideal System from Classical and Density Functional Theories (No.24) Several versions of classical binary nucleation theory (CBNT) were compared with density functional theory (DFT) results for a nonideal model system that mimics the properties of water-ethanol mixtures. The classical theories are distinguished by the absence or presence of a compositional surface tension derivative (CDST) in the Kelvin equations that are usually solved to determine the critical nucleus composition and size. DFT results for a model water-ethanol system were used as the standard against which the classical results were to be judged. Neither of the competing versions of CBNT was entirely satisfactory, which points out the necessity of relying on nonclassical microscopic approaches, such as DFT, for future insight into the binary nucleation of surface active systems. This work formed part of the Ph. D. thesis (2003) of A. Obeidat. The results were published in the proceedings of the 16th International Conference on Nucleation and Atmospheric Aerosols in Kyoto.

2. Experiments and Modeling of Nucleation and Condensation in Supersonic Nozzles

Binary condensation in supersonic nozzles (No. 7) Supersonic nozzle expansions are the experimental means used to make the nanodroplet aerosols for the SANS scattering studies. An extensive study of binary condensation involving ethanol, propanol, and water in pairwise combinations was published in the *Journal of Chemical Physics*. The results of these experiments provide clear evidence for the mutual enhancement of condensation of each alcohol with water, in contrast with the nearly ideal behavior of the ethanol-propanol system.

Nucleation and growth of D_2O nanodroplet aerosols (No. 20) Work on the modeling of nucleation and droplet growth of D_2O aerosols formed in nozzle expansions was published in the proceedings of the 15th International Conference on Nucleation and Atmospheric Aerosols (Aug. 2000).

Isothermal homogeneous nucleation rate measurements in supersonic nozzles (No. 10) Supersonic nozzles with different expansion rates were used to make the first isothermal nucleation rate measurements as a function of supersaturation with a relatively small error margin in J of ±50%. In the temperature range 210 – 230 K, the measured nucleation rates for D_2O ranged between $4 \cdot 10^{16} < J / \mathrm{cm}^{-3}\mathrm{s}^{-1} < 3 \cdot 10^{17}$. These are the highest nucleation rates ever measured. Use of the first nucleation theorem on these data showed that the number of molecules in the critical cluster n^* is less than10! This work was published as a *Feature Article* in the *Journal of Physical Chemistry A*.

3. Nanodroplet Structure and Small Angle Neutron Scattering (SANS) by Nanodroplets

Aerosol SANS experiments and theory (Nos. 4, 5, 18 and 22) This work was concerned with further development of the theory of small angle neutron scattering from nanodroplet aerosols and its application to the analysis of experimental results. Two major publications appeared in the *Physical Review E*. The first paper presented extensive experimental results on the anisotropy of the measured scattered neutron intensity patterns and demonstrated that this effect is due to a Doppler shift in the momentum of the neutrons scattered by the massive, rapidly moving aerosol particles. The second paper contains a complete theoretical framework for interpreting the experimental scattering results and for performing calculations of the expected scattering patterns using various phenomenological or statistical mechanical models.

Surface enrichment in binary nanodroplets (No. 14) In a major experimental triumph, binary aerosol SANS experiments involving water and butanol demonstrated convincingly that water-rich binary nanodroplets have a core-shell structure—a thin layer of butanol surrounds a water-rich spherical core. This work was published as a *Communication* in *Physical Chemistry Chemical Physics*.

Calculations of nanodroplet microstructure (No. 15, 23, and 25) This work used classical density functional theory (DFT) to take an important step in understanding the composition, structure, and phases of aqueous organic nanodroplets. Calculations showed that nanodroplets formed in water-rich vapors had water rich cores surrounded by pentanol rich shells. Droplets formed in pentanol rich vapors had well-mixed cores covered by a pure pentanol layer. A calculated phase diagram showed where core-shell (CS) and well-mixed (WM) droplet structures occur as a function of vapor phase composition. A notable feature of this diagram is a region in which both types of structures occur. These results on the spatial variation of the densities of pentanol and water in binary nanodroplets are remarkably similar to those found in the aerosol SANS experiments on butanol-water mentioned above. This work was published as a *Communication* in *Physical Chemistry Chemical Physics*.

Archival publications supported by this grant:

Journal articles:

1. Wyslouzil, B.E. and Wilemski, G., "Binary nucleation kinetics. V. Φ-lines and evaporation rate surfaces," *J. Chem. Phys.* **110**, 1202-1211 (1999).

2. Wilemski, G., "Binary nucleation kinetics. IV. Directional properties and cluster concentrations at the saddle point," *J. Chem. Phys.* **110**, 6451-6457 (1999).

3. Hale, B. N. and Wilemski, G., "A scaled nucleation model for ideal binary systems," *Chem. Phys. Lett.* **305**, 263-268 (1999).

4. Wyslouzil, B.E., Wilemski, G., Cheung, J.E., Strey, R. and Barker, J., "Doppler shift anisotropy in small angle neutron scattering," *Phys. Rev. E* **60**, 4330-4335 (1999).

5. Wilemski, G., "Neutron scattering from aerosols: Intraparticle structure factor, Guinier analysis of particle speed, and crossed beam kinematics," *Phys. Rev. E* **61**, 557-564 (2000).

6. Li, J.-S., Maksimov, I.L., and Wilemski, G. "Genuine saddle point and nucleation potential for binary systems," *Phys. Rev. E* **61**, R4710-R4713 (2000), *Rapid Communication*.

7. Wyslouzil, B.E., Heath, C. H., Cheung, J. L., and Wilemski, G., "Binary condensation in a supersonic nozzle," *J. Chem. Phys.* **113**, 7317-7329 (2000).

8. Li, J.-S. and Wilemski, G., "Temperature dependence of a Kelvin model for binary nucleation," *J. Phys. Chem. B* **105**, 11778-11784 (2001).

9. Li, J.-S. and Wilemski, G., "Temperature dependence of droplet nucleation in a Yukawa fluid," *J. Chem. Phys.* **118**, 2845-2852 (2003).

10. Kim, Y. J., Wyslouzil, B. E., Wilemski, G., Wölk, J., Strey, R., "Isothermal nucleation rates in supersonic nozzles and the properties of small water clusters," *Feature Article, J. Phys. Chem. A* **108**, 4365-4377 (2004).

11. Wilemski, G. and Li, J.-S., "Nucleation near the spinodal: Limitations of mean field density functional theory," *J. Chem. Phys.* **121**, 7821-7828 (2004).

12. Obeidat, A., Li, J.-S., and Wilemski, G., "Nucleation rates of water and heavy water using equations of state," *J. Chem. Phys.* **121**, 9510-9516 (2004).

13. Fisenko, S. P. and Wilemski, G., "Kinetics of binary nucleation of vapors in size and composition space," *Phys. Rev. E* **70** 056119/1-8 (2004).

14. Wyslouzil, B.E., Wilemski, G., Strey, R., Heath, C. H., and Dieregsweiler, U., "Experimental evidence for internal structure in aqueous-organic nanodroplets," *Phys. Chem. Chem. Phys.* **8**, 54-57 (2006), *Communication*.

15. Li, J.-S. and Wilemski, G., "A structural phase diagram for model aqueous organic nanodroplets," *Phys. Chem. Chem. Phys.* **8**, 1266-1270 (2006), *Communication*.

16. Wilemski, G. "Volumes of critical bubbles from the nucleation theorem," *J. Chem. Phys.* **125**, 114507/1-4 (2006).

17. Obeidat, A. and Wilemski, G., "Gradient theory of nucleation in polar fluids," *Atmos. Res.* **82**, 481-488 (2006).

Conference Proceedings:

18. Wilemski, G. "Theory of Small Angle Neutron Scattering from Nanodroplet Aerosols," in *Proceedings of the Seventeenth Symposium on Energy Engineering Sciences*, Argonne IL, May 1999 (NTIS CONF-990001) (1999) p. 42.

19. Li, J.-S., Maksimov, I. L. and Wilemski, G., "Genuine Saddle Point in Binary Nucleation Kinetics," in *Nucleation and Atmospheric Aerosols, 2000*, edited by B. Hale and M. Kulmala (American Institute of Physics, New York, 2000) pp. 15-18.

20. Heath, C.H., Streletzky, K.A., Wyslouzil, B.E., and Wilemski, G., "D_2O-H_2O Condensation in Supersonic Nozzles: II. Modeling," in *Nucleation and Atmospheric Aerosols, 2000*, edited by B. Hale and M. Kulmala (American Institute of Physics, New York, 2000) pp. 63-66.

21. Fisenko, S. P. and Wilemski, G., "Binary Nucleation Kinetics In Size And Composition Space,"in *Nucleation and Atmospheric Aerosols, 2000*, edited by B. Hale and M. Kulmala (American Institute of Physics, New York, 2000) pp. 343-346.

22. Wyslouzil, B. E., Wilemski, G., and Strey, R., "Aerosol SANS: A New Method to Probe the Structure of Nanodroplets," in *Nucleation and Atmospheric Aerosols, 2000*, edited by B. Hale and M. Kulmala (American Institute of Physics, New York, 2000) pp. 724-727.

23. Wilemski, G. and Li, J.-S. ``Theoretical Studies of Nanodroplet Formation and Microstructure," in *Proceedings of the Twentieth Symposium on Energy Engineering Sciences*, Argonne IL, May 2002 (OSTI, CONF-2002) (2002) p. 245.

24. Obeidat, A., Li, J.-S.and Wilemski, G., "Binary Nucleation of a Nonideal System from Classical and Density Functional Theories," *Nucleation and Atmospheric Aerosols, 2004*, edited by M. Kasahara and M. Kulmala (Kyoto University Press, Kyoto, 2004) pp. 81-84.

25. Li, J.-S.and Wilemski, G., "Composition and Structure of Binary Aerosol Nanodroplets from Density Functional Theory," in *Nucleation and Atmospheric Aerosols, 2004*, edited by M. Kasahara and M. Kulmala (Kyoto University Press, Kyoto, 2004) pp. 169-172.

26. Obeidat, A.and Wilemski, G., "Nucleation of Polar Fluids from Gradient Theory," in *Nucleation and Atmospheric Aerosols, 2004*, edited by M. Kasahara and M. Kulmala (Kyoto University Press, Kyoto, 2004) pp. 186-189.

Master's Thesis:

27. Raman, S. M., "A Monte Carlo discrete sum (MCDS) approach to calculate the free energies of formation and nucleation rates of methanol clusters," M. S. thesis, University of Missouri-Rolla, (2003).

Ph. D. Thesis:

28. Obeidat, A., "Nucleation theory using equations of state," Ph. D. thesis, University of Missouri-Rolla, (2003).

<u>Personnel supported under this grant</u>:

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